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(54) SOLID OXIDE POROUS MEMBRANE AND ITS MANUFACTURING METHOD

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a solid oxide porous membrane small in the amount of gas leak and usefully used as a catalyst carrying membrane for gas separation or a membrane type reactor, or a base material for a solid oxide fuel cell, and provide the method of manufacturing for the solid oxide porous membrane.
SOLUTION: This solid oxide porous membrane is made from a metal oxide base electrolyte, and has a thickness of 10-1000 μm, a porosity of 10-65%, a mean particle size of 0.001-1 μm, the gas transmission amount of the detection limit or less of a helium leak detector, or nitrogen transmission speed of 1×10-11-5×10-5 mol/m2.sec.Pa. The solid oxide porous membrane is manufactured by dry-wet spinning or casting in a doctor blade process a membrane forming solution comprising a polymer material solution in which metal oxide base electrolyte powder is dispersed, and dipping in a gelling bath to form a membrane, then baking the obtained membrane at 1200-1600°C.

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(54)【発明の名称】　固体酸化物多孔質膜およびその製造法

(57)【要約】
【課題】　ガスリーク量が少なく、ガス分離や膜型反応器用の触媒担持膜あるいは固体酸化物燃料電池の基材などとして有効に用いられる固体酸化物多孔質膜およびその製造法を提供する。
【解決手段】　金属酸化物系電解質からなり、膜厚が10～1000μm、気孔率が10～65%、平均孔径が0.001～1μmで、ガス透過量がヘリウムリークディテクタの検出限界以下または窒素透過速度が1×10^{-11}～5×10^{-5}モル/m^2・秒・Paである固体酸化物多孔質膜。この固体酸化物多孔質膜は、金属酸化物系電解質粉末を分散させた高分子物質溶液よりなる製膜原液を乾湿式紡糸しあるいはドクターナイフ法によってキャストし、ゲル化浴に浸せきすることによって得られる膜を1200～1600℃で焼成することによって製造される。

【特許請求の範囲】

【請求項１】　金属酸化物系電解質からなり、膜厚が10～1000μm、気孔率が10～65%、平均孔径が0.001～1μmで、ガス透過量がヘリウムリークディテクタの検出限界以下または窒素透過速度が1×10^{-11}～5×10^{-5}モル/m^2・秒・Paである固体酸化物多孔質膜。

【請求項２】　金属酸化物系電解質がイットリアまたはスカンジアを含有する安定化ジルコニアである請求項１記載の固体酸化物多孔質膜。

【請求項３】　外径が1～6mmの中空糸膜である請求項１記載の固体酸化物多孔質膜。

【請求項４】　平膜である請求項１記載の固体酸化物多孔質膜。

【請求項５】　ガス分離または膜型反応器用の触媒担持膜の基材として用いられる請求項１記載の固体酸化物多孔質膜。

【請求項６】　固体電解質燃料電池用の基材として用いられる請求項１記載の固体酸化物多孔質膜。

【請求項７】　金属酸化物系電解質粉末を分散させた高分子物質溶液よりなる製膜原液を、凝固性液体を芯液として乾湿式紡糸し、ゲル化浴に浸せきすることによって得られる中空糸膜を1200～1600℃で焼成することを特徴とする請求項１に記載された固体酸化物多孔質中空糸膜の製造法。

【請求項８】　金属酸化物系電解質粉末を分散させた高分子物質溶液よりなる製膜原液を、凝固性液体を芯液として乾湿式紡糸し、ゲル化浴に浸せきすることによって得られる中空糸膜を、片端について斜めにカットした後、1200～1600℃で焼成することを特徴とする固体酸化物多孔質中空糸膜の製造法。

【請求項９】　金属酸化物系電解質がイットリアまたはスカンジアを含有する安定化ジルコニアである請求項７または８記載の固体酸化物多孔質中空糸膜の製造法。

【請求項10】　平均粒子径が2μm以下の金属酸化物系電解質粉末が用いられる請求項７または８記載の固体酸化物多孔質中空糸膜の製造法。

【請求項11】　金属酸化物系電解質粉末を分散させた高分子物質溶液よりなる製膜原液をドクターナイフ法でキャストし、ゲル化浴に浸せきすることによって得られる平膜を1200～1600℃で焼成することを特徴とする請求項１に記載された固体酸化物多孔質平膜の製造法。

【請求項12】　金属酸化物系電解質がイットリアまたはスカンジアを含有する安定化ジルコニアである請求項11記載の固体酸化物多孔質平膜の製造法。

【請求項13】　平均粒子径が2μm以下の金属酸化物系電解質粉末が用いられる請求項11記載の固体酸化物多孔質平膜の製造法。

【請求項14】　固体酸化物多孔質中空糸膜の内表面に燃料極を、外表面に空気極を担持させ、各々の電極に電線を取り付けて作製された固体酸化物燃料電池。

【請求項15】　固体酸化物多孔質中空糸膜として片端斜めカット中空糸膜が用いられた請求項14記載の固体酸化物燃料電池。

【請求項16】　固体酸化物多孔質平膜の一方の面に燃料極を、また他方の面に空気極を担持させ、各々の電極に電線を取り付けて作製された固体酸化物燃料電池。

【請求項17】　燃料極がNiOまたはNiO/YSZ電極であり、空気極が$La_{0.8}Sr_{0.2}MnO_3$電極である請求項14または16記載の固体酸化物燃料電池。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、固体酸化物多孔質膜およびその製造法に関する。更に詳しくは、ガス分離や膜型反応器あるいは固体酸化物燃料電池などの分野で有効に用いられる固体酸化物多孔質膜およびその製造法に関する。

【０００２】

【従来の技術】ジルコニアにイットリアまたはスカンジアを含有させた安定化ジルコニアは、高融点、高強度で高靱性であり、高温での化学的安定性も高い。また、高温で酸素イオン透過性を持つ固体電解質としての性質を有する。このことから、安定化ジルコニア多孔質体は、固体酸化物燃料電池用の基材、ガス分離または酸素センサなど膜型反応器用の触媒担持膜の基材としての用途が期待されている。

【０００３】従来技術におけるジルコニア成形体の製造法としては、押出法によるもの(特開平3-183658号公報、同4-37646号公報、同6-116027号公報、同8-264197号公報、特表平8-507896号公報)やドクターブレード法によるもの(特開平7-240217号公報)などがある。しかしながら、これらの方法は、高価な金型やプレス機械が必要で、生産性が低く、また薄膜化が困難であるといった問題があり、平膜や管状の膜を製造することは可能であるが、装置単位容積当りの反応量を高める中空糸膜とすることは困難であった。

【０００４】

【発明が解決しようとする課題】本発明の目的は、ガスリーク量が少なく、ガス分離や膜型反応器用の触媒担持膜あるいは固体酸化物燃料電池の基材などとして有効に用いられる固体酸化物多孔質膜およびその製造法を提供することにある。

【０００５】

【課題を解決するための手段】本発明によって、金属酸化物系電解質からなり、膜厚が10～1000μm、気孔率が10～65%、平均孔径が0.001～1μmで、ガス透過量がヘリウムリークディテクタの検出限界以下または窒素透過速度が1×10^{-11}～5×10^{-5}モル/m^2・秒・Paである固体酸化物多孔質膜が提供され、多孔質膜は中空糸膜状、平膜状などであり得る。

【０００６】固体酸化物多孔質膜は、金属酸化物系電解

質粉末を分散させた高分子物質溶液よりなる製膜原液を乾湿式紡糸しあるいはドクターナイフ法によってキャストし、ゲル化浴に浸せきすることによって得られる膜を1200～1600℃で焼成することによって製造される。

【０００７】

【発明の実施の形態】ジルコニア系粉末、セリア系粉末、ランタンガレート系粉末等が用いられる金属酸化物系電解質粉末は、粒子径が大きいと焼結し難くなることから、平均粒子径が2μm以下のものが好んで用いられる。また、粉末は、製膜原液中20～85重量%、好ましくは55～75重量%の濃度で用いられる。これ以下の濃度では焼結体が得られず、一方これ以上の濃度では中空糸膜の形成が困難となる。

【０００８】製膜原液の調製に用いられる高分子物質としては、有機溶媒に溶解し、熱分解性であれば任意のものを用いることができ、例えばポリスルホン、ポリアミドイミド、ポリエーテルイミド、ポリアクリロニトリル、酢酸セルロース等が用いられる。これらの高分子物質は、製膜原液中4～20重量%、好ましくは6～12重量%の割合で用いられる。これ以下の濃度では中空糸膜の形成が困難となり、一方これ以上の濃度では製膜原液の粘度が高くなり、製膜できなくなる。

【０００９】これらの高分子物質を溶解させる有機溶媒としては、高分子物質を溶解させるものであれば任意のものを用いることができるが、例えばジメチルホルムアミド、ジエチルホルムアミド、ジメチルアセトアミド、ジエチルアセトアミド、ジメチルスルホキシド、N-メチル-2-ピロリドン等の非プロトン性極性溶媒が好んで用いられる。

【００１０】これらの各成分からなる製膜原液は、室温での粘度が約1～10Pa・sと低く、製膜原液中からの気泡の除去が容易に行えるため、焼成後の固体酸化物中にピンホール等が発生し難い。また、それの押出は、通常の圧力容器に製膜原液を満たし、これに約0.05～0.5MPaの圧力を印加することが可能であって、押出に高価な装置を必要とはせず、押出速度も約5～15m/分と速く、量産性に優れている。このような製膜原液を用いての製膜は、凝固性液体、一般には水によって代表される水性液体を芯液として乾湿式紡糸しあるいはドクターナイフ法によってキャストし、ゲル化浴に浸せきすることによって行われる。

【００１１】ここで、中空糸膜を固体酸化物燃料電池として用いる場合には、紡糸後には湿潤状態で複合膜片端部をカッターなどを用いて斜めにカットすることが好ましい。これは、通常の中空糸は管状であり、内表面電極と電線の接合が煩雑な作業となるため、中空糸の端を斜めにカットすることによって中空糸の内表面が外部に曝されるようにすることを目的として行われる。カットする部分は電極との接合がスムーズに行える長さが確保されれば足り、特に限定されないが、通常約10～20mm程度である。紡糸後の中空糸膜は湿潤状態でしなやかであるため任意の形状、例えばU字管形状などに曲げることができ、またカットしても変形はほとんど見られない。

【００１２】この湿潤状態の中空糸膜を1200～1600℃、好ましくは1250～1500℃で焼成することによって、固体酸化物多孔質中空糸膜を与える。焼成温度がこれよりも低いと、中空糸膜の焼結が不十分となって気孔率が大きくなり、機械的強度が損なわれ、一方これよりも高い温度で焼成してもガス透過性は変化しないので、エネルギー的にはロスである。また、焼成時間は1～12時間程度が好ましく、これよりも短かい場合または長い場合は、それぞれ焼成温度が低い場合あるいは高い場合と同様の結果となる。なお、中空糸膜の端をカットしたものについても焼成が行われるが、焼成後についても変形はほとんどみられない。

【００１３】このようにして得られる固体酸化物中空糸膜は、気孔率が10～65%、平均孔径が0.001～1μmと多孔質体であるにも拘らず、ガス透過量がヘリウムリークディテクタの検出限界以下または窒素透過速度が1×10^{-11}～5×10^{-5}モル/m²・秒・Paとガスリーク量が少ない。また、紡糸時のノズル形状を変更することにより、任意形状の中空糸膜を得ることができる。しかしながら、膜厚が薄すぎると中空糸膜の強度は弱くなり、外径が小さいと焼成時に中空糸膜形状の維持が困難となり、一方外径が大きいと紡糸が困難となるので、膜厚は約10～1000μm、外径は約1～6mmであることが好ましい。また、ガスリーク量の調節は、製膜原液の組成、焼成の温度と時間などを調節することによって可能である。

【００１４】かかる固体酸化物中空糸膜は、例えば中空糸膜の管の内側表面に燃料極(例えばNiOまたはNiO/YSZ)を、外側表面に空気極(例えば$La_{0.8}Sr_{0.2}MnO_3$)を担持し、各々の電極に電線を取り付け、この電線に負荷をつなげて電池構成とすることにより燃料電池として有効に用いられる。なお、この燃料電池は、700～1000℃に加熱した状態で、内側に水素、一酸化炭素あるいはメタン等の燃料を、外側に酸素あるいは空気を流すことで発電する。

【００１５】また、固体酸化物多孔質膜は、中空糸膜状ばかりではなく、平膜状、ハニカム膜状等にも成形することができる。平膜状の場合には、その一方の面側に燃料極(NiOまたはNiO/YSZ電極など)を、また他方の面に空気極($La_{0.8}Sr_{0.2}MnO_3$電極など)を担持させ、各々の電極に電線を取り付けることで固体酸化物燃料電池を形成させることができる。

【００１６】この燃料電池は、約700～1000℃に加熱した状態で、燃料極側にH_2、CO、CH_4等の燃料を、また空気極側にO_2あるいは空気を流すことで発電する。

【００１７】

【発明の効果】本発明によって、多孔質体でありながらガス透過量がヘリウムリークディテクタの検出限界以下

または窒素透過速度が1×10^{-11}～5×10^{-5}モル/m^2・秒・Paとガスリーク量の少ない固体酸化物膜が提供される。これは、セラミックスとしてジルコニアを用いて作製した対称構造の中空糸膜は、焼結の進行と共に部分的に緻密化が進行し、気孔率や平均孔径から予測される従来のアルミナ中空糸膜の場合などよりもガスリーク量の少ない中空糸膜が形成されることを示している。

【0018】このような性質を示す本発明の固体酸化物多孔質中空糸膜は、ガス分離または膜型反応器用の触媒担持膜の基材あるいは固体酸化物燃料電池の電極担持基材などとして有効に用いられる。特に、固体酸化物燃料電池の電極担持基材として用いられる場合には、中空糸であるが故に内外径を調節することで同一膜厚の平膜より破断強度を大きくすることができ、また容積が小さいため、昇温時や降温時の固体酸化物内の温度差が小さく、熱膨張差に基づく破壊が抑制されるといった特徴を有する。この場合、中空糸の端を斜めにカットすることにより、中空糸膜の内表面が外部に曝され、内部電極と電線との接合が容易になるといった効果を奏する。さらに、平膜状としても、同様目的に用いることができる。

【0019】

【実施例】次に、実施例について本発明を説明する。

【0020】実施例1

イットリア含有ジルコニア粉末(第一稀元素化学工業製品HSY-8；イットリアY_2O_3含有量8モル%、平均粒子径0.24μm)500g、ポリスルホン(UCC社製品P-1700)40gおよびジメチルホルムアミド200gの混合物からなる製膜原液を、内管径1.2mm、外径3.3mmの二重環状ノズルを用い、芯液(水)流量45ml/分、製膜原液流量20ml/分、ノズル吐出口-ゲル化浴間距離5cm、ゲル化浴(水)温度25℃、紡糸速度10m/分の条件下で乾湿式紡糸し、外径2.0mm、膜厚300μmの複合中空糸膜を得た。

【0021】得られた中空糸膜を5℃/分の昇温速度で昇温し、1400℃で1時間焼成することによって、外径1.8mm、膜厚250μmの真直ぐな安定化ジルコニア中空糸膜を得た。この中空糸膜について、水銀ポロシメーター法で測定すると、気孔率11%、平均孔径0.1μmであった。また、測定温度100℃、供給圧力150kPa、透過側圧力100kPaの条件下で窒素ガス単体の透過速度を測定すると、1×10^{-10}モル/m^2・秒・Paという値が得られた。

【0022】実施例2

イットリア含有ジルコニア粉末(HSY-8)300g、ポリスルホン(P-1700)30gおよびジメチルホルムアミド200gの混合物からなる製膜原液を、内管径1.2mm、外径3.3mmの二重環状ノズルを用い、芯液(水)流量45ml/分、製膜原液流量20ml/分、ノズル吐出口-ゲル化浴間距離5cm、ゲル化浴(水)温度25℃、紡糸速度15m/分の条件下で乾湿式紡糸し、外径2.0mm、膜厚300μmの複合中空糸膜を得た。

【0023】得られた複合中空糸膜を5℃/分の昇温速度で昇温し、1400℃で1時間焼成することによって、外径1.8mm、膜厚250μmの真直ぐな安定化ジルコニア中空糸膜を得た。この中空糸膜について、水銀ポロシメーター法で測定すると、気孔率30%、平均孔径0.1μmであった。また、測定温度100℃、供給圧力150kPa、透過側圧力100kPaの条件下で窒素透過速度を測定すると、4×10^{-9}モル/m^2・秒・Paという値が得られた。

【0024】実施例3

イットリア含有ジルコニア粉末(同社製品HSY-8；イットリアY_2O_3含有量8モル%、平均粒子径1μm)500g、ポリスルホン(P-1700)80gおよびジメチルホルムアミド350gの混合物からなる製膜原液を、内管径2.5mm、外径4.0mmの二重環状ノズルを用い、芯液(水)流量80ml/分、製膜原液流量40ml/分、ノズル吐出口-ゲル化浴間距離5cm、ゲル化浴(水)温度25℃、紡糸速度5m/分の条件下で乾湿式紡糸し、外径3.6mm、膜厚250μmの中空糸膜を得た。

【0025】得られた中空糸膜を5℃/分の昇温速度で昇温し、1400℃で2時間焼成することによって、外径2.4mm、膜厚150μmの真直ぐな安定化ジルコニア中空糸膜を得た。この中空糸膜について、水銀ポロシメーター法で測定すると、気孔率37%、平均孔径0.2μmであった。また、測定温度100℃、供給圧力150kPa、透過側圧力100kPaの条件下で窒素透過速度を測定すると、1×10^{-7}モル/m^2・秒・Paという値が得られた。

【0026】実施例4

実施例3で得られた中空糸膜を5℃/分の昇温速度で昇温し、1450℃で8時間焼成することによって、外径2.4mm、膜厚150μmの真直ぐな安定化ジルコニア中空糸膜を得た。この中空糸膜について、水銀ポロシメーター法で測定すると、気孔率21%、平均孔径0.1μmであった。また、測定温度100℃、供給圧力150kPa、透過側圧力100kPaの条件下で窒素透過速度を測定すると、3×10^{-9}モル/m^2・秒・Paという値が得られた。

【0027】実施例5

実施例3で得られた中空糸膜を5℃/分の昇温速度で昇温し、1500℃で8時間焼成することによって、外径2.4mm、膜厚150μmの真直ぐな安定化ジルコニア中空糸膜を得た。この中空糸膜について、水銀ポロシメーター法で測定すると、気孔率17%、平均孔径0.06μmであった。また、測定温度100℃、供給圧力150kPa、透過側圧力100kPaの条件下で窒素透過速度を測定すると、1×10^{-10}モル/m^2・秒・Paという値が得られた。

【0028】実施例6

実施例1で得られた湿潤状態の中空糸膜を長さ45cmに切断した後、カッターを用いて斜めにカットした。その後、得られた複合中空糸膜を5℃/分の昇温速度で昇温し、1400℃で1時間焼成することによって、外径1.8mm、膜厚250μmの真直ぐな安定化ジルコニア中空糸膜を得た。この中空糸膜について、水銀ポロシメーター法で測定すると、気孔率11%、平均孔径0.1μmであった。また、測定温度100℃、供給圧力150kPa、透過側圧力100kP

aの条件下で窒素ガス単体の透過速度を測定すると、1×10⁻¹⁰モル/m²・秒・Paという値が得られた。

【0029】このようにして得られた安定化ジルコニア中空糸膜の内表面にNiO/YSZ電極を、外表面に$La_{0.8}Sr_{0.2}MnO_3$電極を担持後、各々の電極に電線を取り付けることで、固体電解質燃料電池を作製した。

【0030】実施例7

スカンジア含有ジルコニア粉末(同社製品ScSZ；スカンジアSc_2O_3含有量11モル％、平均粒子径0.6μm)450g、ポリスルホン(P-1700)40gおよびジメチルホルムアミド200gの混合物からなる製膜原液を、内管径1.0mm、外径3.0mmの二重環状ノズルを用い、芯液(水)流量45ml/分、製膜原液流量20ml/分、ノズル吐出口－ゲル化浴間距離5cm、ゲル化浴(水)温度25℃、紡糸速度12m/分の条件下で乾湿式紡糸し、外径1.8mm、膜厚300μmの中空糸膜を得た。

【0031】得られた中空糸膜を5℃/分の昇温速度で昇温し、1250℃で1時間焼成することによって、外径1.6mm、膜厚250μmの真直ぐな安定化ジルコニア中空糸膜を得た。この中空糸膜について、マイクロメリテックス製ポアライザ9310を用いて測定すると、気孔率45％、平均粒径0.1μm、比表面率5m²/gであった。また、測定温度100℃、供給圧力150kPa、透過側圧力100kPaの条件下で窒素ガス単体の透過速度を測定すると、1.5×10^{-5}モル/m²・秒・Paという値が得られた。

【0032】実施例8

イットリア含有ジルコニア粉末(東ソー製品TZ8Y；イットリアY_2O_3含有量8モル％、平均粒子径0.6μm)500g、ポリスルホン(P-1700)40gおよびジメチルホルムアミド200gの混合物からなる製膜原液を、内管径1.2mm、外径3.3mmの二重環状ノズルを用い、芯液(水)流量45ml/分、製膜原液流量20ml/分、ノズル吐出口－ゲル化浴間距離5cm、ゲル化浴(水)温度25℃、紡糸速度10m/分の条件下で乾湿式紡糸し、外径2.0mm、膜厚300μmの中空糸膜を得た。

【0033】得られた中空糸膜を5℃/分の昇温速度で昇温し、1250℃で1時間焼成することによって、外径1.8mm、膜厚250μmの真直ぐな安定化ジルコニア中空糸膜を得た。この中空糸膜について、マイクロメリテックス製ポアライザ9310を用いて測定すると、気孔率50％、平均粒径0.1μm、比表面率4m²/gであった。また、測定温度100℃、供給圧力150kPa、透過側圧力100kPaの条件下で窒素ガス単体の透過速度を測定すると、2×10^{-5}モル/m²・秒・Paという値が得られた。

【0034】実施例9

イットリア含有ジルコニア粉末(TZ8Y)500g、ポリスルホン(P-1700)40gおよびジメチルホルムアミド200gの混合物からなる製膜原液を、内管径1.2mm、外径3.3mmの二重環状ノズルを用い、芯液(水)流量45ml/分、製膜原液流量20ml/分、ノズル吐出口－ゲル化浴間距離5cm、ゲル化浴(水)温度25℃、紡糸速度10m/分の条件下で乾湿式紡糸し、外径2.2mm、膜厚300μmの中空糸膜を得た。

【0035】得られた中空糸膜を5℃/分の昇温速度で昇温し、1300℃で1時間焼成することによって、外径2.0mm、膜厚250μmの真直ぐな安定化ジルコニア中空糸膜を得た。この中空糸膜について、マイクロメリテックス製ポアライザ9310を用いて測定すると、気孔率40％、平均粒径0.1μm、比表面率4m²/gであった。

【0036】実施例10

実施例9で得られた湿潤状態の中空糸膜を長さ30cmに切断した後、カッターを用いて先端が30°の角度になるように斜めにカットした。その後、得られた複合中空糸膜を5℃/分の昇温速度で昇温し、1300℃で1時間焼成することによって、外径2.0mm、膜厚250μmの真直ぐな安定化ジルコニア中空糸膜を得た。この中空糸膜について、マイクロメリテックス製ポアライザ9310を用いて測定すると、気孔率40％、平均粒径0.1μm、比表面率4m²/gであった。

【0037】実施例11

イットリア含有ジルコニア粉末(TZ8Y)500g、ポリスルホン(P-1700)40gおよびジメチルホルムアミド200gの混合物からなる製膜原液を、ドクターナイフを用いてキャストした後、直ちに25℃のゲル化浴(水)中に浸せきし、厚さ300μmの平膜を得た。

【0038】得られた平膜を5℃/分の昇温速度で昇温し、1300℃で1時間焼成することによって、厚さ250μmの平らな安定化ジルコニア平膜を得た。この平膜について、マイクロメリテックス製ポアライザ9310を用いて測定すると、気孔率40％、平均粒径0.1μm、比表面率4m²/gであった。

【0039】実施例12

スカンジア含有ジルコニア粉末(ScSZ)450g、ポリスルホン(P-1700)40gおよびジメチルホルムアミド200gの混合物からなる製膜原液を、内管径1.0mm、外径3.0mmの二重環状ノズルを用い、芯液(水)流量45ml/分、製膜原液流量20ml/分、ノズル吐出口－ゲル化浴間距離5cm、ゲル化浴(水)温度25℃、紡糸速度12m/分の条件下で乾湿式紡糸し、外径1.8mm、膜厚300μmの中空糸膜を得た。

【0040】得られた中空糸膜を5℃/分の昇温速度で昇温し、1300℃で1時間焼成することによって、外径1.6mm、膜厚250μmの真直ぐな安定化ジルコニア中空糸膜を得た。この中空糸膜について、マイクロメリテックス製ポアライザ9310を用いて測定すると、気孔率40％、平均粒径0.1μm、比表面率4m²/gであった。

【0041】実施例9、10、12で得られた安定化ジルコニア中空糸膜の内表面にNiO/YSZ電極を、また外表面に$La_{0.8}Sr_{0.2}MnO_3$電極を担持後、各々の電極に電線を取り付けることで、固体酸化物燃料電池を作製した。また、実施例11で得られた安定化ジルコニア平膜の一方の面にNiO/YSZ電極を、また他方の面に$La_{0.8}Sr_{0.2}MnO_3$電極を担持後、各々の電極に電線を取り付けることで、固体酸化物燃料電池を作製した。

【００４２】実施例13
イットリア含有ジルコニア粉末(TZ8Y)500g、ポリスルホン(P-1700)40gおよびジメチルホルムアミド200gの混合物からなる製膜原液を、内管径1.2mm、外径3.3mmの二重環状ノズルを用い、芯液(水)流量45ml/分、製膜原液流量20ml/分、ノズル吐出ロ-ゲル化浴間距離5cm、ゲル化浴(水)温度25℃、紡糸速度10m/分の条件下で乾湿式紡糸し、外径2.2mm、膜厚300μmの中空糸膜を得た。

【００４３】得られた中空糸膜を5℃/分の昇温速度で昇温し、1500℃で12時間焼成することによって、外径2.0mm、膜厚250μmの真直ぐな安定化ジルコニア中空糸膜を得た。この中空糸膜について、マイクロメリテックス製ポアライザ9310を用いて測定すると、気孔率13%、平均粒径0.04μm、比表面率1m²/gであった。また、島津製作所ヘリウムリークディテクタでヘリウムガスのリーク量を測定したところ、有効膜面積10cm²で、検出感度(3×10⁻¹¹ Pa・m³/秒)以下のリーク量であった。

【００４４】実施例14
実施例13で得られた湿潤状態の中空糸膜を長さ30cmに切断した後、カッターを用いて先端が30゜の角度になるように斜めにカットした。その後、得られた中空糸膜を5℃/分の昇温速度で昇温し、1500℃で12時間焼成することによって、外径2.0mm、膜厚250μmの真直ぐな安定化ジルコニア中空糸膜を得た。この中空糸膜について、マイクロメリテックス製ポアライザ9310を用いて測定すると、気孔率13%、平均粒径0.04μm、比表面率1m²/gであった。また、島津製作所ヘリウムリークディテクタでヘリウムガスのリーク量を測定したところ、有効膜面積10cm²で、検出感度(3×10⁻¹¹ Pa・m³/秒)以下のリーク量であった。

【００４５】実施例15
イットリア含有ジルコニア粉末(TZ8Y)500g、ポリスルホン(P-1700)40gおよびジメチルホルムアミド200gの混合物からなる製膜原液を、ドクターナイフを用いてキャストした後、直ちに25℃のゲル化浴(水)中に浸せきし、厚さ300μmの平膜を得た。

【００４６】得られた平膜を5℃/分の昇温速度で昇温し、1500℃で12時間焼成することによって、肉厚250μmの平らな安定化ジルコニア平膜を得た。この平膜について、マイクロメリテックス製ポアライザ9310を用いて測定すると、気孔率13%、平均孔径0.04μm、比表面率1m²/gであった。また、島津製作所ヘリウムリークディテクタでヘリウムガスのリーク量を測定したところ、有効膜面積10cm²で、検出感度(3×10⁻¹¹ Pa・m³/秒)以下のリーク量であった。

【００４７】実施例16
スカンジア含有ジルコニア粉末(ScSZ)450g、ポリスルホン(P-1700)40gおよびジメチルホルムアミド200gの混合物からなる製膜原液を、内管径1.0mm、外径3.0mmの二重環状ノズルを用い、芯液(水)流量45ml/分、製膜原液流量20ml/分、ノズル吐出ロ-ゲル化浴間距離5cm、ゲル化浴(水)温度25℃、紡糸速度12m/分の条件下で乾湿式紡糸し、外径1.8mm、膜厚300μmの中空糸膜を得た。

【００４８】得られた中空糸膜を5℃/分の昇温速度で昇温し、1500℃で12時間焼成することによって、外径1.6mm、膜厚250μmの真直ぐな安定化ジルコニア中空糸膜を得た。この中空糸膜について、マイクロメリテックス製ポアライザ9310を用いて測定すると、気孔率11%、平均孔径0.03μm、比表面率1m²/gであった。また、島津製作所ヘリウムリークディテクタでヘリウムガスのリーク量を測定したところ、有効膜面積10cm²で、検出感度(3×10⁻¹¹ Pa・m³/秒)以下のリーク量であった。

フロントページの続き

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CLAIMS

[Claim(s)]
[Claim 1] Solid acid ghost porous membrane below the limit of detection of a helium leak detector or whose nitrogen transmission rate it consists of a metallic-oxide system electrolyte, and the amount of gas transparency is [thickness / 10-1000 micrometers and porosity] 1x10-11 - 5x10 -five-mol [/m] 2, a second, and Pa in 0.001-1 micrometer for 10 - 65%, and an average aperture.
[Claim 2] Solid acid ghost porous membrane according to claim 1 which is the fully stabilized zirconia in which a metallic-oxide system electrolyte contains yttria or scandia.
[Claim 3] Solid acid ghost porous membrane according to claim 1 which is a hollow fiber whose outer diameter is 1-6mm.
[Claim 4] Solid acid ghost porous membrane according to claim 1 which is a flat film.
[Claim 5] Solid acid ghost porous membrane according to claim 1 used as a base material of the catalyst support film for gas separation or membrane type reactors.
[Claim 6] Solid acid ghost porous membrane according to claim 1 used as a base material for solid electrolyte fuel cells.
[Claim 7] The manufacturing method of the solid acid ghost porosity hollow fiber indicated by claim 1 characterized by calcinating the hollow fiber obtained by carrying out dryness-and-moisture type spinning, using a freezing characteristic liquid as core liquid, and carrying out the dipping of the film production undiluted solution which consists of a high polymer solution which distributed metallic-oxide system electrolyte powder to a gelation bath at 1200-1600 degrees C.
[Claim 8] The manufacturing method of the solid acid ghost porosity hollow fiber characterized by calcinating it at 1200-1600 degrees C after cutting aslant the hollow fiber obtained by carrying out dryness-and-moisture type spinning, using a freezing characteristic liquid as core liquid, and carrying out the dipping of the film production undiluted solution which consists of a high polymer solution which distributed metallic-oxide system electrolyte powder to a gelation bath about one end.
[Claim 9] The manufacturing method of the solid acid ghost porosity hollow fiber according to claim 7 or 8 which is the fully stabilized zirconia in which a metallic-oxide system electrolyte contains yttria or scandia.
[Claim 10] The manufacturing method of the solid acid ghost porosity hollow fiber according to claim 7 or 8 for which metallic-oxide system electrolyte powder 2 micrometers or less is used for mean particle diameter.
[Claim 11] The manufacturing method of the solid acid ghost porosity flat film indicated by claim 1 characterized by calcinating the flat film obtained by carrying out the cast of the film production undiluted solution which consists of a high polymer solution which distributed metallic-oxide system electrolyte powder by the doctor knife method, and carrying out a dipping to a gelation bath at 1200-1600 degrees C.
[Claim 12] The manufacturing method of the solid acid ghost porosity flat film according to claim 11 which is the fully stabilized zirconia in which a metallic-oxide system electrolyte contains yttria or scandia.

[Claim 13] The manufacturing method of the solid acid ghost porosity flat film according to claim 11 for which metallic-oxide system electrolyte powder 2 micrometers or less is used for mean particle diameter.
[Claim 14] The solid acid ghost fuel cell which support a fuel electrode to the internal surface of a solid acid ghost porosity hollow fiber, and the outside surface was made to support an air pole, and attached the electric wire in each electrode and was produced.
[Claim 15] The solid acid ghost fuel cell according to claim 14 with which the one end slanting cut hollow fiber was used as a solid acid ghost porosity hollow fiber.
[Claim 16] The solid acid ghost fuel cell which support a fuel electrode to one field of a solid acid ghost porosity flat film, and the field of another side was made to support an air pole, and attached the electric wire in each electrode and was produced.
[Claim 17] The solid acid ghost fuel cell according to claim 14 or 16 whose fuel electrode is NiO or a NiO/YSZ electrode and whose air pole is La0.8 Sr0.2 MnO3 electrode.

[Translation done.]

* NOTICES *

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to solid acid ghost porous membrane and its manufacturing method. Furthermore, it is related with the solid acid ghost porous membrane effectively used in detail in fields, such as gas separation, and a membrane type reactor or a solid acid ghost fuel cell, and its manufacturing method.
[0002]
[Description of the Prior Art] The fully stabilized zirconia which made the zirconia contain yttria or scandia is high toughness in high-melting and high intensity, and its chemical stability in an elevated temperature is also high. Moreover, it has a property as a solid electrolyte which has oxygen ionic permeability at an elevated temperature. From this, as for the fully-stabilized-zirconia porous body, the application as a base material of catalyst support film for membrane type reactors, such as a base material for solid acid ghost fuel cells, gas separation, or an oxygen sensor, is expected.
[0003] As a manufacturing method of the zirconia Plastic solid in the conventional technique, there are what is depended on an extrusion method (JP,3-183658,A, a 4-37646 official report, a 6-116027 official report, a 8-264197 official report, Patent Publication Heisei No. 507896 [eight to] official report), a thing (JP,7-240217,A) to depend on a doctor blade method. However, expensive metal mold and an expensive press machine were required for these approaches, and although it was possible for there to have been a problem that thin-film-izing is difficult, and to have manufactured a flat film and the tubing-like film low [productivity], it was difficult [it] to consider as the hollow fiber which raises the reacting weight per equipment unit volume.
[0004]
[Problem(s) to be Solved by the Invention] The purpose of this invention has few amounts of gas leaks, and is to offer the solid acid ghost porous membrane effectively used as gas separation, a base material of the catalyst support film for membrane type reactors, or a solid acid ghost fuel cell, etc., and its manufacturing method.
[0005]
[Means for Solving the Problem] By this invention, it consists of a metallic-oxide system electrolyte, the solid acid ghost porous membrane below the limit of detection of a helium leak detector or whose nitrogen transmission rate the amount of gas transparency is [thickness / 10-1000 micrometers and porosity] 1x10-11 - 5x10 -five-mol [/m] 2, a second, and Pa in 0.001-1 micrometer for 10 - 65% and an average aperture is offered, and porous membrane may have the shape of the shape of a hollow fiber, and a flat film etc.
[0006] Solid acid ghost porous membrane is manufactured by calcinating the film obtained by carrying out dryness-and-moisture type spinning of the film production undiluted solution which consists of a high polymer solution which distributed metallic-oxide system electrolyte powder, or carrying out the cast and carrying out a dipping to a gelation bath by the doctor knife method at 1200-1600 degrees C.
[0007]

[Embodiment of the Invention] If the metallic-oxide system electrolyte powder with which zirconia system powder, the Seria system powder, lanthanum gallate system powder, etc. are used has large particle diameter, since it will be hard coming to sinter, a thing 2 micrometers or less is fond, and mean particle diameter is used. Moreover, powder is preferably used by 55 - 75% of the weight of concentration 20 to 85% of the weight among a film production undiluted solution. In the concentration not more than this, a sintered compact is not obtained but, on the other hand, formation of a hollow fiber becomes difficult by the concentration beyond this.
[0008] It dissolves in an organic solvent, as a high polymer used for preparation of a film production undiluted solution, if it is pyrolysis nature, the thing of arbitration can be used, for example, polysulfone, polyamidoimide, polyether imide, a polyacrylonitrile, cellulose acetate, etc. are used. These high polymers are preferably used at 6 - 12% of the weight of a rate four to 20% of the weight among a film production undiluted solution. Formation of a hollow fiber becomes difficult, and the viscosity of a film production undiluted solution becomes high, and it becomes impossible to produce a film with the concentration beyond this on the other hand by the concentration not more than this.
[0009] Although the thing of arbitration can be used as an organic solvent in which these high polymers are dissolved if a high polymer is dissolved, aprotic polar solvents, such as dimethylformamide, a diethyl formamide, dimethylacetamide, a diethyl acetamide, dimethyl sulfoxide, and a N-methyl-2-pyrrolidone, are fond, and are used, for example.
[0010] The film production undiluted solution which consists of each of these components has the viscosity as low as about one to 10 Pa-s in a room temperature, and since removal of the air bubbles out of a film production undiluted solution can carry out easily, a pinhole etc. cannot generate it easily in the solid acid ghost after baking. Moreover, the extrusion of that can impress the pressure of about 0.05 to 0.5 MPa to this, does not need expensive equipment for extrusion, but fills a film production undiluted solution to the usual pressurized container, and is [its extrusion rate is also as quick as a part for about 5-15m/, and] excellent in mass-production nature. Film production using such a film production undiluted solution is performed by carrying out dryness-and-moisture type spinning, using as core liquid a freezing characteristic liquid and the aquosity liquid generally represented bywater, or carrying out the cast and carrying out a dipping to a gelation bath by the doctor knife method.
[0011] Here, when using a hollow fiber as a solid acid ghost fuel cell, it is desirable to use the bipolar membrane one end section by the damp or wet condition, to use a cutter etc. after spinning, and to cut aslant. This of the usual hollow filament is tubular, and since junction of an internal-surface electrode and an electric wire serves as a complicated activity, it is performed for the purpose of the internal surface of a hollow filament being put outside by cutting the edge of a hollow filament aslant. Although it is sufficient for the part to cut if the die length which can perform junction to an electrode smoothly is secured, and not limited especially, it is usually about about 10-20mm. Most deformation is not seen even if it can be bent since the hollow fiber behind spinning is pliant, the configuration, for example, the U tube configuration etc., of arbitration etc., and it cuts it by the damp or wet condition.
[0012] A solid acid ghost porosity hollow fiber is given by calcinating preferably 1200-1600 degrees C of hollow fibers of this damp or wet condition at 1250-1500 degrees C. Since gas permeability will not change even if sintering [of a hollow fiber] becomes inadequate, porosity becomes large, a mechanical strength is spoiled and it calcinates at temperature higher than this on the other hand if burning temperature is lower than this, it is a loss in energy. Moreover, about 1 - 12 hours of firing time are desirable, and a short paddle case or when long, the result same when burning temperature is low respectively as the case of being high is brought from this. In addition, baking is performed about what cut the edge of a hollow fiber, and most deformation is not seen about the baking back, either.
[0013] Thus, as for the solid acid ghost hollow fiber obtained, although porosity is [10 - 65% and an average aperture] 0.001-1 micrometer and a porous body, below the limit of detection of a helium leak detector or a nitrogen transmission rate has [the amount of gas transparency] few 1x10-11 - 5x10 -five-mol [/m] 2, seconds and Pa, and amounts of gas leaks. Moreover, the hollow fiber of an arbitration configuration can be obtained by changing the nozzle dimensions at the time of spinning. However, since the reinforcement of a hollow fiber will become weak if thickness is too thin, maintenance of a

hollow fiber configuration will become difficult at the time of baking if an outer diameter is small, and spinning will become difficult on the other hand if an outer diameter is large, it is desirable that thickness is about 10-1000 micrometers, and an outer diameter is about 1-6mm. Moreover, accommodation of the amount of gas leaks is possible by adjusting temperature, time amount, etc. of the presentation of a film production undiluted solution, and baking.

[0014] A fuel electrode (for example, NiO or NiO/YSZ) is supported on the inside front face of tubing of a hollow fiber, it supports an air pole (for example, La0.8 Sr0.2 MnO3) on an outside front face, and this solid acid ghost hollow fiber attaches an electric wire in each electrode, and is effectively used as a fuel cell by tying a load to this electric wire and considering as a cell configuration. In addition, this fuel cell is in the condition heated at 700-1000 degrees C, and is generated by pouring fuels, such as hydrogen, a carbon monoxide, or methane, inside, and pouring oxygen or air outside.

[0015] Moreover, solid acid ghost porous membrane can be fabricated not only the shape of a hollow fiber but the shape of the shape of a flat film, and honeycomb film etc. a flat film-like case -- the field side of one of these -- fuel electrodes (NiO or NiO/YSZ electrode) -- moreover, the field of another side can be made to be able to support air poles (La0.8 Sr0.2 MnO3 electrode etc.), and a solid acid ghost fuel cell can be made to form by attaching an electric wire in each electrode

[0016] This fuel cell is in the condition heated at about 700-1000 degrees C, and is generated by pouring the fuel of H2, CO, and CH4 grade to a fuel electrode side, and pouring O2 or air to an air pole side.

[0017]

[Effect of the Invention] By this invention, though it is a porous body, the solid acid ghost film with few below the limit of detection of a helium leak detector or the nitrogen transmission rates in 1x10-11 - 5x10 -five-mol [/m] 2, a second and Pa, and the amount of gas leaks is offered for the amount of gas transparency. Eburnation advances partially with advance of sintering and the hollow fiber of the symmetry structure which produced this, using a zirconia as ceramics shows that a hollow fiber with few amounts of gas leaks than the case of the conventional alumina hollow fiber predicted from porosity or an average aperture etc. is formed.

[0018] The solid acid ghost porosity hollow fiber of this invention which shows such a property is effectively used as the base material of the catalyst support film for gas separation or membrane type reactors, or an electrode support base material of a solid acid ghost fuel cell. When especially used as an electrode support base material of a solid acid ghost fuel cell, although it is a hollow filament therefore, breaking strength can be made larger than the flat film of the same thickness by adjusting the diameter of inside and outside, and since the volume is small, it has the description that the temperature gradient in the solid acid ghost at the time of a temperature up and a temperature fall is small, and the destruction based on a differential thermal expansion is controlled. In this case, by cutting the edge of a hollow filament aslant, the internal surface of a hollow fiber is put outside and does so the effectiveness that junction on an internal electrode and an electric wire becomes easy. Furthermore, it can use for the purpose similarly as the shape of a flat film.

[0019]

[Example] Next, this invention is explained about an example.

[0020] example 1 yttria content zirconia powder (Daiichi Kigenso Kagaku Kogyo product HSY-8; 2Oyttria Y3 content % of eight mols --) The film production undiluted solution which consists of mixture (mean-particle-diameter [of 0.24 micrometers / of 500g], and polysulfone (UCC product P-1700) 40g, and dimethylformamide 200g) A duplex annular nozzle with 1.2mm [of diameters of an inner tube] and an outer diameter of 3.3mm is used. A part for core liquid(water) flow rate/of 45ml, Dryness-and-moisture type spinning was carried out under the distance between a part for /, and film production undiluted solution flow rate nozzle delivery [of 20ml]-gelation baths of 5cm, the gelation bath(water) temperature of 25 degrees C, and 10m conditions for /in spinning rate, and the outer diameter of 2.0mm and the compound hollow fiber of 300 micrometers of thickness were obtained.

[0021] The outer diameter of 1.8mm and the straight fully-stabilized-zirconia hollow fiber of 250 micrometers of thickness were obtained by carrying out the temperature up of the obtained hollow fiber with 5-degree-C programming rate for /, and calcinating at 1400 degrees C for 1 hour. When measured

by the mercury-porosimeter method about this hollow fiber, they were 11% of porosity, and 0.1 micrometers of average apertures. Moreover, when the transmission rate of a nitrogen gas simple substance was measured under the conditions of the measurement temperature of 100 degrees C, supply-pressure 150kPa, and transparency lateral pressure 100kPa, the value of 1x10 -ten-mol [/m] 2, a second, and Pa was acquired.

[0022] The film production undiluted solution which consists of mixture (300g [of example 2 yttria content zirconia powder] (HSY-8), and polysulfone (P-1700) 30g, and dimethylformamide 200g) A duplex annular nozzle with 1.2mm [of diameters of an inner tube] and an outer diameter of 3.3mm is used. A part for core liquid(water) flow rate/of 45ml, Dryness-and-moisture type spinning was carried out under the distance between a part for /, and film production undiluted solution flow rate nozzle delivery [of 20ml]-gelation baths of 5cm, the gelation bath(water) temperature of 25 degrees C, and 15m conditions for /in spinning rate, and the outer diameter of 2.0mm and the compound hollow fiber of 300 micrometers of thickness were obtained.

[0023] The outer diameter of 1.8mm and the straight fully-stabilized-zirconia hollow fiber of 250 micrometers of thickness were obtained by carrying out the temperature up of the obtained compound hollow fiber with 5-degree-C programming rate for /, and calcinating at 1400 degrees C for 1 hour. When measured by the mercury-porosimeter method about this hollow fiber, they were 30% of porosity, and 0.1 micrometers of average apertures. Moreover, when the nitrogen transmission rate was measured under the conditions of the measurement temperature of 100 degrees C, supply-pressure 150kPa, and transparency lateral pressure 100kPa, the value of 4x10 -nine-mol [/m] 2, a second, and Pa was acquired.

[0024] example 3 yttria content zirconia powder (company product HSY-8; 2Oyttria Y3 content % of eight mols --) The film production undiluted solution which consists of mixture (mean-particle-diameter [of 1 micrometer / of 500g], and polysulfone (P-1700) 80g, and dimethylformamide 350g) A duplex annular nozzle with 2.5mm [of diameters of an inner tube] and an outer diameter of 4.0mm is used. A part for core liquid(water) flow rate/of 80ml, Dryness-and-moisture type spinning was carried out under the distance between a part for /, and film production undiluted solution flow rate nozzle delivery [of 40ml]-gelation baths of 5cm, the gelation bath(water) temperature of 25 degrees C, and 5m conditions for /in spinning rate, and the outer diameter of 3.6mm and the hollow fiber of 250 micrometers of thickness were obtained.

[0025] The outer diameter of 2.4mm and the straight fully-stabilized-zirconia hollow fiber of 150 micrometers of thickness were obtained by carrying out the temperature up of the obtained hollow fiber with 5-degree-C programming rate for /, and calcinating at 1400 degrees C for 2 hours. When measured by the mercury-porosimeter method about this hollow fiber, they were 37% of porosity, and 0.2 micrometers of average apertures. Moreover, when the nitrogen transmission rate was measured under the conditions of the measurement temperature of 100 degrees C, supply-pressure 150kPa, and transparency lateral pressure 100kPa, the value of 1x10 -seven-mol [/m] 2, a second, and Pa was acquired.

[0026] The outer diameter of 2.4mm and the straight fully-stabilized-zirconia hollow fiber of 150 micrometers of thickness were obtained by carrying out the temperature up of the hollow fiber obtained in the example 4 example 3 with 5-degree-C programming rate for /, and calcinating at 1450 degrees C for 8 hours. When measured by the mercury-porosimeter method about this hollow fiber, they were 21% of porosity, and 0.1 micrometers of average apertures. Moreover, when the nitrogen transmission rate was measured under the conditions of the measurement temperature of 100 degrees C, supply-pressure 150kPa, and transparency lateral pressure 100kPa, the value of 3x10 -nine-mol [/m] 2, a second, and Pa was acquired.

[0027] The outer diameter of 2.4mm and the straight fully-stabilized-zirconia hollow fiber of 150 micrometers of thickness were obtained by carrying out the temperature up of the hollow fiber obtained in the example 5 example 3 with 5-degree-C programming rate for /, and calcinating at 1500 degrees C for 8 hours. When measured by the mercury-porosimeter method about this hollow fiber, they were 17% of porosity, and 0.06 micrometers of average apertures. Moreover, when the nitrogen transmission rate

was measured under the conditions of the measurement temperature of 100 degrees C, supply-pressure 150kPa, and transparency lateral pressure 100kPa, the value of 1x10 -ten-mol [/m] 2, a second, and Pa was acquired.
[0028] After cutting the hollow fiber of the damp or wet condition acquired in the example 6 example 1 in die length of 45cm, it cut aslant using the cutter. Then, the outer diameter of 1.8mm and the straight fully-stabilized-zirconia hollow fiber of 250 micrometers of thickness were obtained by carrying out the temperature up of the obtained compound hollow fiber with 5-degree-C programming rate for /, and calcinating at 1400 degrees C for 1 hour. When measured by the mercury-porosimeter method about this hollow fiber, they were 11% of porosity, and 0.1 micrometers of average apertures. Moreover, when the transmission rate of a nitrogen gas simple substance was measured under the conditions of the measurement temperature of 100 degrees C, supply-pressure 150kPa, and transparency lateral pressure 100kPa, the value of 1x10 -ten-mol [/m] 2, a second, and Pa was acquired.
[0029] Thus, the solid electrolyte fuel cell was produced by attaching a NiO/YSZ electrode in the internal surface of the obtained fully-stabilized-zirconia hollow fiber, and attaching an electric wire in each electrode after supporting La0.8 Sr0.2 MnO3 electrode to an outside surface.
[0030] example 7 scandia content zirconia powder (company product ScSZ; 2Oscandia Sc3 content % of 11 mols --) The film production undiluted solution which consists of mixture (mean-particle-diameter [of 0.6 micrometers / of 450g], and polysulfone (P-1700) 40g, and dimethylformamide 200g) A duplex annular nozzle with 1.0mm [of diameters of an inner tube] and an outer diameter of 3.0mm is used. A part for core liquid(water) flow rate/of 45ml, Dryness-and-moisture type spinning was carried out under the distance between a part for /, and film production undiluted solution flow rate nozzle delivery [of 20ml]-gelation baths of 5cm, the gelation bath(water) temperature of 25 degrees C, and 12m conditions for /in spinning rate, and the outer diameter of 1.8mm and the hollow fiber of 300 micrometers of thickness were obtained.
[0031] The outer diameter of 1.6mm and the straight fully-stabilized-zirconia hollow fiber of 250 micrometers of thickness were obtained by carrying out the temperature up of the obtained hollow fiber with 5-degree-C programming rate for /, and calcinating at 1250 degrees C for 1 hour. When measured about this hollow fiber using the Micromeritics pore riser 9310, it was porosity [of 45%], mean-particle-diameter [of 0.1 micrometers], and rate of specific surface 5m2/g. Moreover, when the transmission rate of a nitrogen gas simple substance was measured under the conditions of the measurement temperature of 100 degrees C, supply-pressure 150kPa, and transparency lateral pressure 100kPa, the value of 1.5x10 -five mols /, m2, a second, and Pa was acquired.
[0032] example 8 yttria content zirconia powder (TOSOH product TZ8Y; 2Oyttria Y3 content % of eight mols --) The film production undiluted solution which consists of mixture (mean-particle-diameter [of 0.6 micrometers / of 500g], and polysulfone (P-1700) 40g, and dimethylformamide 200g) A duplex annular nozzle with 1.2mm [of diameters of an inner tube] and an outer diameter of 3.3mm is used. A part for core liquid(water) flow rate/of 45ml, Dryness-and-moisture type spinning was carried out under the distance between a part for /, and film production undiluted solution flow rate nozzle delivery [of 20ml]-gelation baths of 5cm, the gelation bath(water) temperature of 25 degrees C, and 10m conditions for /in spinning rate, and the outer diameter of 2.0mm and the hollow fiber of 300 micrometers of thickness were obtained.
[0033] The outer diameter of 1.8mm and the straight fully-stabilized-zirconia hollow fiber of 250 micrometers of thickness were obtained by carrying out the temperature up of the obtained hollow fiber with 5-degree-C programming rate for /, and calcinating at 1250 degrees C for 1 hour. When measured about this hollow fiber using the Micromeritics pore riser 9310, it was porosity [of 50%], mean-particle-diameter [of 0.1 micrometers], and rate of specific surface 4m2/g. Moreover, when the transmission rate of a nitrogen gas simple substance was measured under the conditions of the measurement temperature of 100 degrees C, supply-pressure 150kPa, and transparency lateral pressure 100kPa, the value of 2x10 -five mols /, m2, a second, and Pa was acquired.
[0034] The film production undiluted solution which consists of mixture (500g [of example 9 yttria content zirconia powder] (TZ8Y), and polysulfone (P-1700) 40g, and dimethylformamide 200g) A

duplex annular nozzle with 1.2mm [of diameters of an inner tube] and an outer diameter of 3.3mm is used. A part for core liquid(water) flow rate/of 45ml, Dryness-and-moisture type spinning was carried out under the distance between a part for /, and film production undiluted solution flow rate nozzle delivery [of 20ml]-gelation baths of 5cm, the gelation bath(water) temperature of 25 degrees C, and 10m conditions for /in spinning rate, and the outer diameter of 2.2mm and the hollow fiber of 300 micrometers of thickness were obtained.
[0035] The outer diameter of 2.0mm and the straight fully-stabilized-zirconia hollow fiber of 250 micrometers of thickness were obtained by carrying out the temperature up of the obtained hollow fiber with 5-degree-C programming rate for /, and calcinating at 1300 degrees C for 1 hour. When measured about this hollow fiber using the Micromeritics pore riser 9310, it was porosity [of 40%], mean-particle-diameter [of 0.1 micrometers], and rate of specific surface 4m2/g.
[0036] After cutting the hollow fiber of the damp or wet condition acquired in the example 10 example 9 in die length of 30cm, it cut aslant so that a tip might become the include angle which is 30 degrees using a cutter. Then, the outer diameter of 2.0mm and the straight fully-stabilized-zirconia hollow fiber of 250 micrometers of thickness were obtained by carrying out the temperature up of the obtained compound hollow fiber with 5-degree-C programming rate for /, and calcinating at 1300 degrees C for 1 hour. When measured about this hollow fiber using the Micromeritics pore riser 9310, it was porosity [of 40%], mean-particle-diameter [of 0.1 micrometers], and rate of specific surface 4m2/g.
[0037] After carrying out the cast of the film production undiluted solution which consists of mixture (500g [of example 11 yttria content zirconia powder] (TZ8Y), and polysulfone (P-1700) 40g, and dimethylformamide 200g) using a doctor knife, the dipping was immediately carried out during the 25-degree C gelation bath(water), and the flat film with a thickness of 300 micrometers was obtained.
[0038] The even fully-stabilized-zirconia flat film with a thickness of 250 micrometers was obtained by carrying out the temperature up of the obtained flat film with 5-degree-C programming rate for /, and calcinating at 1300 degrees C for 1 hour. When measured about this flat film using the Micromeritics pore riser 9310, it was porosity [of 40%], mean-particle-diameter [of 0.1 micrometers], and rate of specific surface 4m2/g.
[0039] The film production undiluted solution which consists of mixture (450g [of example 12 scandia content zirconia powder] (ScSZ), and polysulfone (P-1700) 40g, and dimethylformamide 200g) A duplex annular nozzle with 1.0mm [of diameters of an inner tube] and an outer diameter of 3.0mm is used. A part for core liquid(water) flow rate/of 45ml, Dryness-and-moisture type spinning was carried out under the distance between a part for /, and film production undiluted solution flow rate nozzle delivery [of 20ml]-gelation baths of 5cm, the gelation bath(water) temperature of 25 degrees C, and 12m conditions for /in spinning rate, and the outer diameter of 1.8mm and the hollow fiber of 300 micrometers of thickness were obtained.
[0040] The outer diameter of 1.6mm and the straight fully-stabilized-zirconia hollow fiber of 250 micrometers of thickness were obtained by carrying out the temperature up of the obtained hollow fiber with 5-degree-C programming rate for /, and calcinating at 1300 degrees C for 1 hour. When measured about this hollow fiber using the Micromeritics pore riser 9310, it was porosity [of 40%], mean-particle-diameter [of 0.1 micrometers], and rate of specific surface 4m2/g.
[0041] The solid acid ghost fuel cell was produced by attaching a NiO/YSZ electrode in the internal surface of the fully-stabilized-zirconia hollow fiber obtained in the examples 9, 10, and 12, and attaching an electric wire in each electrode after supporting La0.8 Sr0.2 MnO3 electrode to an outside surface. Moreover, the solid acid ghost fuel cell was produced by attaching a NiO/YSZ electrode in one field of the fully-stabilized-zirconia flat film obtained in the example 11, and attaching an electric wire in each electrode after supporting La0.8 Sr0.2 MnO3 electrode to the field of another side.
[0042] The film production undiluted solution which consists of mixture (500g [of example 13 yttria content zirconia powder] (TZ8Y), and polysulfone (P-1700) 40g, and dimethylformamide 200g) A duplex annular nozzle with 1.2mm [of diameters of an inner tube] and an outer diameter of 3.3mm is used. A part for core liquid(water) flow rate/of 45ml, Dryness-and-moisture type spinning was carried out under the distance between a part for /, and film production undiluted solution flow rate nozzle

delivery [of 20ml]-gelation baths of 5cm, the gelation bath(water) temperature of 25 degrees C, and 10m conditions for /in spinning rate, and the outer diameter of 2.2mm and the hollow fiber of 300 micrometers of thickness were obtained.
[0043] The outer diameter of 2.0mm and the straight fully-stabilized-zirconia hollow fiber of 250 micrometers of thickness were obtained by carrying out the temperature up of the obtained hollow fiber with 5-degree-C programming rate for /, and calcinating at 1500 degrees C for 12 hours. When measured about this hollow fiber using the Micromeritics pore riser 9310, it was porosity [of 13%], mean-particle-diameter [of 0.04 micrometers], and rate of specific surface 1m2/g. Moreover, when the amount of leaks of gaseous helium was measured by the Shimadzu helium leak detector, it was the amount of leaks below detection sensitivity (3x10-11 Pa-m3/second) in 2 10cm of effective film surface products.
[0044] After cutting the hollow fiber of the damp or wet condition acquired in the example 14 example 13 in die length of 30cm, it cut aslant so that a tip might become the include angle which is 30 degrees using a cutter. Then, the outer diameter of 2.0mm and the straight fully-stabilized-zirconia hollow fiber of 250 micrometers of thickness were obtained by carrying out the temperature up of the obtained hollow fiber with 5-degree-C programming rate for /, and calcinating at 1500 degrees C for 12 hours. When measured about this hollow fiber using the Micromeritics pore riser 9310, it was porosity [of 13%], mean-particle-diameter [of 0.04 micrometers], and rate of specific surface 1m2/g. Moreover, when the amount of leaks of gaseous helium was measured by the Shimadzu helium leak detector, it was the amount of leaks below detection sensitivity (3x10-11 Pa-m3/second) in 2 10cm of effective film surface products.
[0045] After carrying out the cast of the film production undiluted solution which consists of mixture (500g [of example 15 yttria content zirconia powder] (TZ8Y), and polysulfone (P-1700) 40g, and dimethylformamide 200g) using a doctor knife, the dipping was immediately carried out during the 25-degree C gelation bath(water), and the flat film with a thickness of 300 micrometers was obtained.
[0046] The even fully-stabilized-zirconia flat film with a thickness of 250 micrometers was obtained by carrying out the temperature up of the obtained flat film with 5-degree-C programming rate for /, and calcinating at 1500 degrees C for 12 hours. When measured about this flat film using the Micromeritics pore riser 9310, it was 13% [of porosity], 0.04 micrometer [of average apertures], and rate of specific surface 1m2/g. Moreover, when the amount of leaks of gaseous helium was measured by the Shimadzu helium leak detector, it was the amount of leaks below detection sensitivity (3x10-11 Pa-m3/second) in 2 10cm of effective film surface products.
[0047] The film production undiluted solution which consists of mixture (450g [of example 16 scandia content zirconia powder] (ScSZ), and polysulfone (P-1700) 40g, and dimethylformamide 200g) A duplex annular nozzle with 1.0mm [of diameters of an inner tube] and an outer diameter of 3.0mm is used. A part for core liquid(water) flow rate/of 45ml, Dryness-and-moisture type spinning was carried out under the distance between a part for /, and film production undiluted solution flow rate nozzle delivery [of 20ml]-gelation baths of 5cm, the gelation bath(water) temperature of 25 degrees C, and 12m conditions for /in spinning rate, and the outer diameter of 1.8mm and the hollow fiber of 300 micrometers of thickness were obtained.
[0048] The outer diameter of 1.6mm and the straight fully-stabilized-zirconia hollow fiber of 250 micrometers of thickness were obtained by carrying out the temperature up of the obtained hollow fiber with 5-degree-C programming rate for /, and calcinating at 1500 degrees C for 12 hours. When measured about this hollow fiber using the Micromeritics pore riser 9310, it was 11% [of porosity], 0.03 micrometer [of average apertures], and rate of specific surface 1m2/g. Moreover, when the amount of leaks of gaseous helium was measured by the Shimadzu helium leak detector, it was the amount of leaks below detection sensitivity (3x10-11 Pa-m3/second) in 2 10cm of effective film surface products.

[Translation done.]